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Radiometric Method for the Determination of Uranium in Water: Single-Laboratory Evaluation and Interlaboratory Collaborative Study

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RADIOMETRIC METHOD FOR THE DETERMINATION OF URANIUM IN WATER: Single-Laboratory Evaluation and Interlaboratory Collaborative Study

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound integrated monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs.

This report presents the results of a single-laboratory evaluation and an interlaboratory collaborative study of a method for measuring uranium in water. Such studies are extremely useful as they demonstrate the state-of-the-art of the analytical methodology which will ultimately provide the information for decisions associated with environmental standards and guidelines. Collaborative studies also allow each participating laboratory to critically evaluate its capabilities in comparison with other laboratories and often document the need for taking corrective action to improve techniques. For further information, contact the Methods Development and Analytical Support Branch, Monitoring Systems Research and Development Division, Environmental Monitoring and Support Laboratory, Las Vegas, Nevada.

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

ABSTRACT

The results of a single-laboratory evaluation and an inter-laboratory collaborative study of a method for determining uranium in water are reported. The method consists of coprecipitation of uranium with ferrous hydroxide, a nitric-hydrofluoric acid dissolution if the sample contains sediment, separation of the uranium by anion exchange chromatography, and electrodeposition, followed by alpha pulse height analysis.

Four reference samples, ranging from 1 to 2,000 disintegrations per minute per liter, were prepared for evaluating the method. These samples consisted of two actual environmental samples, a substitute ocean water sample, and a sample containing sediment. Measured uranium concentrations for these samples agreed to within 5% of the reference concentrations, while tracer recoveries averaged about 70%. The precision of the collaborative study results approached counting statistics errors for the three water samples which did not contain sediment.

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The authors would like to thank all those individuals from the participating laboratories involved in the collaborative study (cf. Appendix 4).

Several people at Mound Facility provided support for the present study. Thanks are due to Warren E. Sheehan, F. Keith Tomlinson and Billy M. Farmer for providing the necessary sample counting services and to Charles A. Phillips, Paul E. Figgins and Bobby Robinson for helpful discussions and suggestions.

INTRODUCTION

This study was designed to choose and evaluate a method which could be recommended for measuring uranium isotopes in environmental water samples and in aqueous discharges from nuclear facilities. The determination of uranium in environmental samples is becoming more important with the increased operations of nuclear power plants and the mining and milling of uranium ores. Isotopic uranium analysis can be used to determine uranium-234/uranium-238 ratios in environmental samples and for monitoring effluents from U-235 enrichment plants. Other non-naturally produced uranium isotopes found in aqueous samples can be identified and measured. Examples are U-234 produced from decay of plutonium-238, and U-233 which will be produced in large quantities if thorium-232 is converted to U-233 in breeder reactors.

For recommendation, the method would have to be applicable to a variety of water samples in the concentration range of a few tenths to several thousand disintegrations per minute per liter. The method would also have to produce results of sufficient precision and accuracy, be free of interferences from other alpha-emitting radionuclides, and be applicable to the routine analysis of large numbers of samples.

SUMMARY

A candidate method to determine the concentration of uranium isotopes in water has been developed at the Mound Facility, Miamisburg, Ohio. This report presents the results of a single-laboratory evaluation and interlaboratory collaborative study of this method. Support for this work was provided by EPA's Environmental Monitoring and Support Laboratory-Las Vegas, Nevada under the terms of an "Interagency Agreement."

After an extensive literature search of currently available methods and preliminary laboratory testing, a method was chosen for further evaluation. Criteria were established for the method, subject to EPA approval, and a single-laboratory evaluation was used to confirm that these criteria were met. The single-laboratory evaluation was performed using actual wastewater samples from Mound Facility and from a uranium processing

facility and with samples prepared for the subsequent inter-laboratory collaborative test.

A copy of the procedure (Appendix I) and duplicates of four different water samples were sent to eleven laboratories which had agreed to participate in the collaborative study. Two of these samples were taken from actual effluents discharged to the environment and the third sample was "substitute ocean water" to which a known amount of uranium was added. The fourth sample consisted of "diluted pitchblende ore" of a known uranium concentration which was added to a liter of deionized water. The participants were also supplied with a standard U-232 tracer to eliminate error due to standardization of the tracer by the participating laboratories. Eight laboratories had submitted results after a 5-month period. Data from seven of these laboratories were acceptable and a statistical evaluation of the collaborative study was carried out.

CONCLUSIONS

The single-laboratory evaluation demonstrated that the uranium-in-water procedure met the requirements set forth in the criteria established for the method. Chemical recoveries averaged about 70%, and the accuracy and precision of the method were shown to be acceptable. Interlaboratory collaborative study results agreed with the reference values to within 5% for the determinations of higher level samples where counting statistics errors were not a major factor. The precision of the results approached that of counting statistics for the water samples not containing sediment. Although the precisions observed for the sample containing sediment were somewhat higher than counting statistics error, good agreement with the reference values was obtained. Uranium activities as low as 0.1 disintegrations per minute per liter (dpm/l) were measured, and plutonium, thorium, americium and polonium tracer activities (10 to 100 dpm) and lead (15 mg) did not interfere with the uranium determinations. The method was shown to be applicable for water samples to which "diluted pitchblende ore" was added. However, in order to show that the present procedure is applicable to a particular environmental water sample containing sediment, it would be advisable to analyze the water portion of the sample by the present method and the sediment by an appropriate uranium-in-soil method and to compare the sum of these determinations with the analysis of the total sample by the present procedure.

From the conclusions presented, the authors believe that the method described in this report provides a relatively simple and accurate means of determining uranium isotopes in water.

CRITERIA

Criteria were established for the present method based on the information obtained from a review of published methods used for the determination of uranium in water.

The criteria were as follows:

1. The method will be an alpha pulse-height analysis method, rather than a chemical method giving only total uranium.

2. Simplicity of equipment, reagents and procedure will be emphasized to reflect cost effectiveness.

3. The chemical yield of the method will be 50% or greater.

4. The method will apply to filtered water samples and to water samples containing sediment.

5. The method shall be applicable to up to 20 liters of fresh water or seawater.

6. Plutonium, americium, thorium, lead and polonium tracers will be used in testing the method to give assurance that isotopes of these elements do not interfere with the uranium analysis.

7. The sensitivity of the method with 1-liter samples will be 0.1 dpm/l or better.

8. The single-laboratory relative standard deviation of the method, not including the counting statistics error, will be 5% or better.

9. The accuracy of the method will be dependent upon the pipetting accuracy, the accuracy of the tracer (U-232) to be used, and the counting errors. The overall uncertainty of the tracer is expected to be about 1.5%.

CHOICE OF METHOD

One of the criteria for the method was that alpha pulse-height analysis should be used for detection of the uranium isotopes. Prior to alpha pulse-height analysis, the uranium had to be preconcentrated from solution, separated from the other elements present, and prepared for counting.

For preconcentration of uranium from water samples, three procedures are commonly used: coprecipitation, adsorption on charcoal, or ion exchange. Of these three methods, coprecipitation was chosen because it was the easiest and least time consuming, although cation exchange gives high recoveries for samples of up to 600 liters (Veselsky 1974). While several coprecipitation methods could have been used (Hodge et al., 1974; Edwards, 1968), coprecipitation of the uranium with ferrous hydroxide had been previously shown* to give high recoveries and, therefore, was selected as a means of preconcentrating the uranium. For effective coprecipitation of the uranium, it is essential that carbon dioxide be removed from the sample prior to precipitation and that carbonate-free reagents (fresh ammonium hydroxide) are used to prevent the formation of a carbonate complex ion of uranium in basic solution. To make the procedure applicable to water samples containing sediment, an acid dissolution, similar to that used in a soil analysis (USAEC, 1974), was added to the procedure to analyze such samples.

Ion exchange chromatography was found to be an extensively used and easily implemented means of isolating the uranium for subsequent electrodeposition on stainless steel slides (Korkisch, et al., 1974, 1975a, 1975b, 1976). An electrodeposition procedure similar to those previously published (Puphal and Olsen, 1972; Talvitie, 1971) was shown to give good results in a method for determination of plutonium in water (Bishop et al., 1978). This procedure was shown to work well for uranium also, and electrodeposition time could be reduced from 2 hours to 1 hour. As previously stated, alpha pulse-height analysis, using a silicon surface barrier detector, was used for counting the uranium activity which was electrodeposited onto stainless steel slides. Uranium-232 was chosen for use as a tracer because its alpha energy is considerably higher than other uranium isotopes of interest in environmental samples.

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*Sill, C. W., private communication, Health Services Laboratory, Department of Energy, Idaho Falls, Idaho. 1977

PREPARATION OF REFERENCE MATERIALS

Four reference materials were prepared for procedure evaluation and also for use in the collaborative study. Two water samples were taken from actual water discharged to the environment and, after filtration through Whatman GF/C paper, they were acidified to 0.5M with concentrated nitric acid. The first environmental sample, labeled 77-1 and referred to as Sample 1, was a wastewater sample from a uranium processing facility. This sample had a uranium-238 concentration of about 2,000 dpm/l and also contained other natural radioisotopes in addition to the uranium isotopes. The second environmental sample, labeled 77-2 and referred to as Sample 2, was wastewater discharged from Mound Facility. Although the primary contaminant in this water was plutonium-238, it also contained uranium-233 at concentrations of about 10 dpm/l. The reference concentrations for these samples were obtained by many repeated determinations and appropriate statistical analysis.

The other two materials were prepared by adding a substance of known uranium concentration to water. The third sample, labeled 77-3 and referred to as Sample 3, was "substitute ocean water" to which a known amount of uranium was added. This sample was prepared by adding a standard uranium solution to substitute ocean water prepared according to an ASTM procedure (ASTM, 1977a). The standard solution was made by dissolving dried (900°C for 1 hour) National Bureau of Standards (NBS) uranium oxide (NBS SRM #950a) in nitric acid, and then diluting it to give a concentration of about 500 dpm/l. The known concentration of this solution was verified by electrodepositing an aliquot with a U-236 solution which had been standardized for Mound by the NBS. About 90 kg of the substitute ocean water was transferred to a 30-gallon polyethylene container. Weighed amounts of concentrated nitric acid (32 ml/liter of water), the uranium standard solution, and saturated lithium chloride solution were added to the water. This solution was mixed for 4 hours with a peristaltic pump having a flow rate of 4 liters/min. The lithium concentration was periodically determined by atomic absorption spectroscopy and complete mixing was verified. Lithium was added because it has a very good sensitivity in atomic absorption analysis and only a small amount had to be added to the water samples. Subsequently 1-liter samples were pumped into polyethylene containers and stored.

The fourth sample, labeled 77-4 and referred to as Sample 4, consisted of individually prepared 0.100-gram samples of diluted pitchblende ore added to about a liter of deionized water. Each sample was preserved with 32 ml of concentrated nitric acid and shaken vigorously. The entire sample was transferred to a beaker when it was to be analyzed. This ore was supplied by the Environmental Monitoring and Support Laboratory-Las Vegas, Nevada, and the uranium concentration had been determined at the Health Services Laboratory, Idaho Falls, Idaho.

SINGLE-LABORATORY EVALUATION

The method was evaluated at Mound Facility before the multilaboratory collaborative study was begun. Also, since the concentration of the uranium isotopes in Samples 1 and 2 were unknown, these samples were analyzed many times in order to obtain reference values for the uranium concentrations. The results of these analyses are summarized in Table 1 through 4. The average uranium recovery observed for multiple analysis of the four samples was 71 ± 10%. The average values determined for Samples 1 and 2 were used for the reference values in the subsequent collaborative study. However, since Samples 3 and 4 were prepared from standards of known uranium concentrations, the concentrations calculated from the known values were used as reference values. A few analyses of Samples 3 and 4 were carried out to assure that the present method was capable of analyzing these samples, and these results are also listed. An ASTM-recommended criterion, which is discussed in the next section of this report, was used for rejection of outliers (ASTM, 1977b).

Thorium-230, polonium-210, plutonium-236 and americium-243 tracers were used in evaluating the procedure for effective chemical separation of the uranium from these elements. When each of the four tracers (10 to 100 dpm) was added to the samples which were analyzed for uranium by the present procedure, it was found that no detectable tracer (<1%) was observed in the final alpha spectrum. When stable lead (15 milligrams) was added to the sample, no detectable lead (<1%) was found by atomic absorption spectroscopy in the final solution to be electrodeposited.

The uranium recovery efficiency of the ferrous hydroxide coprecipitation procedure was evaluated for up to 20-liter water samples. Even though 500 mg of iron was used for coprecipitation of uranium from 20-liter samples, tracer recoveries were less consistent, ranging from 10 to 66%, and lower, yielding an average recovery of about 35%, than for 1-liter samples.

TABLE 1. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 1 (Uranium Processing Facility Effluent)

Sample	U-238 (dpm/l)	U-234,-233 (dpm/l)	U-235,-236 (dpm/l)	Recovery %
1A	2003	1553	117	92
1B	2093	1598	114	86
1C	2119	1577	96	90
1D	2070	1596	128	84
1E	2133	1644	154	82
1F	2081	1638	150	75
1G	2091	1663	150	84
Avg.	2085 ± 42	1610 ± 40	130 ± 22	85 ± 6

TABLE 2. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 2 (Mound Facility Effluent)

Sample	U-238 (dpm/l)	U-234,-233 (dpm/l)	U-235,-236 (dpm/l)	Recovery %
2A	0.024	13.90	0.10	61
2B	0.11	12.89	0.097	86
2C	0.042	11.36*	0.053	94
2D	0.12	13.69	0.13	71
2E	0.065	13.17	0.019	54
2F	0.23	12.87	0.12	75
2G	0.086	13.68	0.097	75
2H	--[a]	14.14	--[a]	81
2I	--[a]	14.14	--[a]	60
2J	--[a]	13.86	--[a]	31
2K	0.14	14.02	0.19	79
2L	0.10	13.65	0.11	91
Avg.	0.10 ± 0.06	13.62 ± 0.46	0.102 ± 0.048	72 ± 18

*Rejected by ASTM test.

[a]Alpha spectrum not completely resolved.

TABLE 3. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 3 (Substitute Ocean Water)

Sample	U-238 (dpm/l)	U-234,-233 (dpm/l)	U-235,-236 (dpm/l)	Recovery (%)
3A	1.75	1.65	0.110	54
3B	1.76	1.72	0.086	65
3C	1.72	1.73	0.065	64
3D	1.71	1.71	0.081	82
Avg.	1.73 ± 0.03	1.70 ± 0.04	0.086 ± 0.019	66 ± 12
Ref.	1.73 ± 0.02	1.73 ± 0.02	0.080 ± 0.002	

TABLE 4. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 4 (Sample Containing Sediment)

Sample	U-238 (dpm/l)	U-234,-233 (dpm/l)	U-235,-236 (dpm/l)	Recovery (%)
4A	54.2	56.6	2.71	65
4B	59.0	59.2	--[a]	61
Avg.	56.6 ± 3.4	57.9 ± 1.7	2.71	63 ± 3
Ref.	56.2 ± 0.4	56.2 ± 0.4	2.63 ± 0.08	

[a]Alpha spectrum not completely resolved.

INTERLABORATORY COLLABORATIVE STUDY

On the basis of the single-laboratory evaluation, a multi-laboratory collaborative study was carried out to validate the effectiveness of the proposed method under a variety of user conditions. The procedure to be used and specific collaborative study instructions were sent to the participating laboratories. Subsequently, about 250 ml of the sample from the uranium processing facility and duplicate 1-liter portions of the other three reference samples were also sent, together with standard U-232 tracer to be used in the analyses. In a previous study (Bishop, et al., 1978), Mound and EPA personnel agreed that analyses which had tracer recoveries of less than 20% would be considered questionable and the resulting data would be omitted from further consideration. Such an extremely low recovery would indicate that there was something seriously wrong with that particular analysis.

After several months, eight of the eleven laboratories which had been sent samples completed the analyses, while more pressing commitments made it impossible for the other laboratories to do the study. Each laboratory was randomly assigned a number from 1 to 8 and the collaborative study results are listed in Tables 5 through 8. Also presented in each of these tables are averages of the replicate results, $\bar{X}$; the experimental standard deviations, S_i; the ratios of the average value to the known value, $\bar{X}/\bar{X}_{Ref}$; and the uranium tracer recovery for each of the analyses. In these tables, determinations which had chemical recoveries of $\leq$ 20% were rejected as unacceptable results, and outliers were rejected on the basis of an ASTM recommended criterion for rejection (ASTM, 1977b).

For this rejection criterion, with n observations listed in order of increasing magnitude by $x_1 \leq x_2 \leq x_3 \leq \ldots \leq x_n$, if the largest value x_n is in question, then T_n is calculated as follows:

$$T_n = (x_n - \bar{x})/s \qquad (1)$$

where:

T_n = test criterion

$\bar{x}$ = arithmetic average of all n values

TABLE 5. COLLABORATIVE STUDY RESULTS FOR SAMPLE 1 (Uranium Processing Facility Effluent - Reference Concentrations: U-238 = 2085 dpm/1; U-234,-233 = 1610 dpm/1; U-235,-236 = 130 dpm/1)

Lab	U-238[b,d] (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	U-234,-233[b] (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	U-235,-236[b] (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	Recovery (%)
1	2153 ± 75 2109 ± 75	2131 ± 31	1.02	1670 ± 63 1702 ± 64	1686 ± 23	1.05	123 ± 15 106 ± 14	115 ± 12	0.89	72 60
3	1800 ± 80* 2000 ± 170*	———	———	1500 ± 70* 1600 ± 140*	———	———	74 ± 10* 96 ± 22*	———	———	19 9
4	2164 ± 37	———[c]	1.04	1734 ± 31	———	1.08	———	———	———	98
5	2080 ± 46 2161 ± 37	2121 ± 57	1.02	1638 ± 38 1662 ± 36	1650 ± 17	1.02	95 ± 6.8 111 ± 7.0	103 ± 11	0.79	91 88
6	2040 ± 97* 1840 ± 45†	———[c]	0.88	1550 ± 76* 1460 ± 38†	———	0.91	———	———	———	10 48
7	2170 ± 43 2220 ± 44	2195 ± 35	1.05	1630 ± 34 1660 ± 35	1645 ± 21	1.02	135 ± 8.9 150 ± 7.9	143 ± 11	1.10	90 87
8	2180 ± 137 1960 ± 106	2070 ± 156	0.99	1840 ± 121 1520 ± 89	1680 ± 226	1.04	95 ± 24 78 ± 18	87 ± 12	0.67	53 76

[a] Where S_i is the experimental (within laboratory) standard deviation; $\bar{X}$ is the average of replicate results; and X_{Ref} is the reference concentration (dpm/1). This also applies to Tables 6 through 8.

[b] The error given here is the error associated with one-sigma counting statistics. This statement also applies to Tables 6 through 8.

[c] When only one uranium concentration was determined, or if one value was rejected, no average or standard deviation is tabulated. This also applies to Tables 6 through 8.

[d] Laboratory 2 did not analyze Sample 1.

*Rejected because uranium tracer recovery was less than 20%.

†Rejected by ASTM test.

TABLE 6. COLLABORATIVE STUDY RESULTS FOR SAMPLE 2 (Mound Facility Effluent - Reference Concentrations: U-238 = 0.10 dpm/l; U-234,-233 = 13.62 dpm/l; U-235,-236 = 0.102 dpm/l)

Lab	U-238 (dpm/l)	$\bar{X} \pm S_i$ (dpm/l)	$\frac{\bar{X}}{X_{Ref}}$	U-234,-233 (dpm/l)	$\bar{X} \pm S_i$ (dpm/l)	$\frac{\bar{X}}{X_{Ref}}$	U-235,-236 (dpm/l)	$\bar{X} \pm S_i$ (dpm/l)	$\frac{\bar{X}}{X_{Ref}}$	Recovery (%)
1	0.048±0.02 0.099±0.03	0.074±0.04	0.7	13.70±0.43 13.43±0.43	13.57±0.19	0.99	0.037±0.017 0.033±0.017	0.033±0.001	0.33	67 69
2	0.18±9.04 0.10±0.04	0.14±0.06	1.4	13.73±0.48 13.08±0.70	13.41±0.46	0.98	0.069±0.025 0.058±0.033	0.064±0.007	0.63	90 46
3	0.21±0.10* 0.20±0.07*	----	----	15±1* 15±1*	----	----	----	----	----	11 18
4	2.03±0.12†	----	----	14.16±0.42	----	1.04	----	----	----	37
5	0.10±0.02	----	1.0	13.46±0.34	----	0.99	----	----	----	77
6	----	----	----	13.86±0.44 14.01±0.48 13.96±0.20 13.72±0.32	13.89±0.13	1.02	----	----	----	39 29 69 68
7	0.15±0.03 0.10±0.02	0.13±0.04	1.3	13.53±0.34 13.51±0.35	13.52±0.02	0.99	----	----	----	83 78
8	0.17±0.05 0.12±0.04	0.15±0.04	1.5	13.57±0.62 12.82±0.52	13.20±0.53	0.97	0.033±0.024 0.013±0.013	0.024±0.014	0.24	31 40

*Rejected because uranium tracer recovery was less than 20%.

†Rejected by ASTM test.

TABLE 7. COLLABORATIVE STUDY RESULTS FOR SAMPLE 3 (Substitute Ocean Water - Reference Concentrations: U-238 = 1.73 dpm/1; U-234,-233 = 1.73 dpm/1; U-235,-236 = 0.080 dpm/1)

Lab	U-238 (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	U-234,-233 (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	U-235,-236 (dpm/1)	$\bar{X} \pm S_i$ (dpm/1)	$\frac{\bar{X}}{X_{Ref}}$	Recovery (%)
1	1.59±0.11 1.71±0.12	1.65±0.08	0.95	1.54±0.11 1.86±0.12	1.70±0.23	0.98	0.146±0.036 0.032±0.017	0.089±0.068	1.11	58 64
2	1.44±0.11 1.71±0.15	1.58±0.19	0.91	1.80±0.13 1.76±0.15	1.78±0.03	1.03	0.037±0.034 0.088±0.035	0.063±0.036	0.79	90 65
3	1.9±0.4* 1.7±0.2*	——	——	2.1±0.4* 1.8±0.2*	——	——	——	——	——	7 17
4	2.10±0.15*	——	——	2.52±0.17*	——	——	——	——	——	16
5	1.75±0.14 1.70±0.13	1.73±0.04	1.00	1.84±9.14 1.61±0.12	1.73±0.16	1.00	0.033±0.017 0.033±0.015	0.033±0.000	0.41	80 80
6	1.61±0.21* 1.52±0.12 1.88±0.10	1.70±0.25	0.98	1.83±0.22* 1.63±0.12 1.69±0.11	1.66±0.04	0.96	——	——	——	11 30 61
7	1.66±0.08 1.90±0.10	1.78±0.17	1.03	1.67±0.08 1.76±0.09	1.72±0.06	0.99	0.085±0.020 ——	——	1.06	85 76
8	1.78±0.16 1.62±0.15	1.70±0.11	0.98	1.78±0.16 1.51±0.15	1.65±0.19	0.95	0.077±0.034 0.107±0.040	0.092±0.021	1.15	97 99

*Rejected because uranium tracer recovery was less than 20%.

TABLE 8. COLLABORATIVE STUDY RESULTS FOR SAMPLE 4 (Sample Containing Sediment - Reference Concentrations: U-238 = 56.2 dpm/sample; U-234,-233 = 56.2 dpm/sample; U-235,-236 = 2.63 dpm/sample)

Lab	U-238 (dpm/ sample)	$\bar{X} \pm S_i$ (dpm/ sample)	$\frac{\bar{X}}{X_{Ref}}$	U-234,-233 (dpm/ sample)	$\bar{X} \pm S_i$ (dpm/ sample)	$\frac{\bar{X}}{X_{Ref}}$	U-235,-236 (dpm/ sample)	$\bar{X} \pm S_i$ (dpm/ sample)	$\frac{\bar{X}}{X_{Ref}}$	Recovery (%)
1	58.6±1.4 58.9±1.4	58.8±0.2	1.05	58.5±1.4 58.3±1.4	58.4±0.1	1.04	2.81±0.15 2.43±0.14	2.62±0.23	1.00	79 78
2	55.8±12.4* 57.5±2.3	——	1.02	65.0±14.3* 57.9±2.3	——	1.03	4.44±1.8* 3.50±0.27	——	1.33	1.6 51
3	57±3* 57±2*	——	——	54±3* 58±2*	——	——	3.3±0.3* 2.6±0.2*	——	——	13 18
4	51.3±1.3	——	0.91	50.7±1.3	——	0.90	——	——	——	57
5	56.1±1.5 56.0±1.8	56.1±0.1	1.00	53.3±1.4 57.0±1.8	55.2±2.6	0.98	2.63±0.17 2.91±0.17	2.77±0.17	1.05	79 78
6	57.2±1.8 54.7±1.5 54.5±1.2	55.5±1.5	0.99	54.3±1.7 54.9±1.5 53.2±1.2	54.1±0.9	0.96				21 36 61
7	57.9±1.4 57.4±1.4	57.7±0.4	1.03	55.8±1.3 56.9±1.4	56.4±0.8	1.00	2.90±0.15 2.90±0.16	2.90±0.00	1.10	87 80
8	40.0±3.4* 51.0±1.2	——	0.91	41.2±3.5* 50.7±1.4	——	0.90	1.48±0.4* 2.41±0.1	——	0.92	17 56

*Rejected because uranium tracer recovery was less than 20%.

s = the estimate of the population standard deviation based on the sample data

Alternately if x_1 rather than x_n is the doubtful value, the criterion is as follows:

$$T_1 = (\bar{x} - x_1)/s \qquad (2)$$

If the T_n or T_1 value exceeds the critical value, the measurement in question may be rejected. Critical values of T for various levels of significance are given in the ASTM reference (ASTM, 1977b). A 5% two-sided level of significance was employed in deciding whether or not to reject a given measurement in the present study.

When a laboratory had made only one determination or when one of the duplicates had been rejected, the one acceptable value was used as the laboratory average. The average value of each laboratory was used in calculating the average collaborative study value. Reference values for Samples 1 and 2 were obtained from the single-laboratory evaluation. All data received from Laboratory 3 had tracer recoveries of $\leq$ 20%; therefore, data from only seven laboratories were included in this study. Only 84.4% of the total alpha branches from U-235 are included in a well-resolved spectrum of natural uranium (Sill, 1977). Since this correction was not included in the collaborative study instructions, the uranium-235 concentrations reported by the laboratories were divided by 0.844. The laboratory calculations were checked to ensure that this correction had not been made previously.

A summary of the collaborative study results is given in Table 9. In this table, average isotopic concentrations that were determined in the collaborative study for each sample are listed along with corresponding reference concentrations. The estimated standard deviations for the reference concentrations, S_{Ref}, and the estimated collaborative study standard deviations, S_d, are also given in Table 9.

The precision standard deviation or the combined within-laboratory standard deviation, S_r, and the standard deviation of the systematic errors or the precision of the method between laboratories, S_b, are also given in Table 9. The precision standard deviation is estimated according to Youden's Formula (3) (Youden and Steiner, 1975) as follows for duplicate determinations:

$$S_r = (\Sigma d^2/2n)^{\frac{1}{2}} \qquad (3)$$

TABLE 9. SUMMARY OF URANIUM-IN-WATER COLLABORATIVE STUDY RESULTS*

Sample	Isotope	Tabulated Quantity (dpm/l, dpm for Sample 4)					
		$\bar{X}_{Ref}$	$\bar{X}_c$	S_{Ref}	S_d	S_r	S_b
1	U-238	2085	2136	42	47	86	-
1	U-234,-233	1610	1679	40	36	115	-
1	U-235,-236	130	112	22	24	12	22
2	U-238	0.10	0.12	0.06	0.03	0.04	0.01
2	U-234,-233	13.62	13.60	0.46	0.32	0.33	0.22
2	U-235,-236	0.102	0.040	0.048	0.021	0.010	0.020
3	U-238	1.73	1.69	0.02	0.07	0.16	-
3	U-234,-233	1.73	1.71	0.02	0.05	0.14	-
3	U-235,-236	0.080	0.073	0.002	0.025	0.045	-
4	U-238	56.2	55.4	0.4	3.1	0.8	3.0
4	U-234,-233	56.2	54.8	0.4	3.1	1.4	2.9
4	U-235,-236	2.63	2.84	0.08	0.41	0.19	0.39

*The tabulated quantities are defined as: $\bar{X}_{Ref}$ - reference concentration, $\bar{X}_c$ - collaborative study average concentration, S_{Ref} - standard deviation of the reference value, S_d - standard deviation of the laboratory averages, S_r - precision standard deviation or combined within-laboratory standard deviation, S_b - standard deviation of the systematic errors or precision of the method between laboratories.

where: d = the absolute difference between the duplicates

n = the number of collaborating laboratories reporting duplicates

The standard deviation of the systematic error, S_b, is computed from the other two standard deviations according to Youden's Formula (4) (Youden and Steiner, 1975):

$$S_b^2 = S_d^2 - S_r^2/2 \qquad (4)$$

It can be seen from Table 9 that the within-laboratory standard deviation, S_r, is the most significant source of error for Samples 1 and 3 of the collaborative study, while the between-laboratory standard deviation, S_b, is insignificant, except for the U-235, -236 determinations of Sample 1. These results can be explained from the data given in Tables 5 through 7. There is a large difference between some of the duplicates, especially for laboratory 8, when compared to the other results, which gave a large value of S_r calculated from equation (3). Since there was a limited amount of duplicate data, a large difference in one of the duplicates resulted in a large value of S_r and a corresponding low value for S_b (equation 4). For Samples 2 and 4 and the U-235, -236 determinations in Sample 1, there were no unusually large differences in the duplicate data which would cause the within-laboratory deviation to be so large that the between-laboratory deviation could not be determined. Therefore, the between-laboratory deviation, S_b, was found to be a main contributor to the experimentally observed standard deviation, S_d, for these determinations.

DISCUSSION OF RESULTS

From the comparison of the average collaborative study uranium concentrations with the reference values shown in Table 9, there appears to be good agreement of the data for all four samples. To determine whether the average collaborative study concentrations agree with the reference values, the t-test was used. Two equations were used in applying the t-test. The first relationship applies to a situation in which the average of the measured value and the average of the reference value each shows a significant standard deviation; this equation is as follows (Walpole and Myers, 1972):

$$t = \left| \bar{X}_c - \bar{X}_{Ref} \right| \Big/ \left(\frac{S_c^2}{n_c} + \frac{S_{Ref}^2}{n_{Ref}} \right)^{\frac{1}{2}} \quad (5)$$

where:

t = test criterion

$\bar{X}_c$ = average of collaborative test results

$\bar{X}_{Ref}$ = average reference value

S_c = estimated standard deviation of collaborative test results

n_c = number of collaborating laboratories

S_{Ref} = estimated standard deviation of reference concentration

n_{Ref} = number of determinations made in obtaining the reference value

The second relationship applies to a situation in which the error in the reference value is considered to be negligible; or, in other words, the reference value is considered to be the true mean. This equation is as follows (Youden and Steiner, 1975):

$$t = \frac{\left| \bar{X}_c - R \right| (n_c)^{\frac{1}{2}}}{S_c} \quad (6)$$

where:

R = the reference value considered to be the true mean

Other quantities are defined as in equation (5)

Equation (5) was used to calculate the t values for Samples 1 and 2, and equation (6) was applied to obtain t values for Samples 3 and 4. The calculated values of t for the four reference samples and the data used to calculate these values are given in Table 10. Critical values of t (t_{crit}), determined for a 5% level of significance, are also given for comparison to the calculated t values. When t is less than t_{crit}, it can be said that the two means agree. It can be seen in Table 10

TABLE 10. t-TEST FOR SYSTEMATIC ERRORS IN COLLABORATIVE STUDY RESULTS

Sample	Isotope	Tabulated Quantity[a]					
		$\bar{X}_c \pm S_c$	$\bar{X}_{Ref} \pm S_{Ref}$	n_c	n_{Ref}	t	t_{crit}
1	U-238	2136 ± 47	2085 ± 42	5	7	1.94	2.23
1	U-234,-233	1679 ± 36	1610 ± 40	5	7	3.12	2.23
1	U-235,-236	112 ± 24	130 ± 22	4	7	1.22	2.26
2	U-238	0.12 ± 0.03	0.10 ± 0.06	5	9	0.43	2.18
2	U-234,-233	13.60 ± 0.32	13.62 ± 0.46	7	12	1.24	2.11
2	U-235,-236	0.040 ± 0.021	0.102 ± 0.048	3	9	2.55	2.23
3	U-238	1.69 ± 0.07	1.73	6	-	1.40	2.57
3	U-234,-233	1.71 ± 0.05	1.73	6	-	0.98	2.57
3	U-235,-236	0.073 ± 0.025	0.080	5	-	1.92	2.78
4	U-238	55.4 ± 3.1	56.2	7	-	0.68	2.45
4	U-234,-233	54.8 ± 3.1	56.2	7	-	1.20	2.45
4	U-235,-236	2.84 ± 0.41	2.63	5	-	1.47	2.78

[a]The tabulated quantities are defined in the text.

that all results from the collaborative study agree with the reference values, except the U-234, -233 determination in Sample 1 and the U-235, -236 determination in Sample 2.

Since the U-235, -236 concentration in Sample 2 was very low and since only three collaborative study results were obtained, the data appear to be inadequate to ascertain if there is a bias in this case. However, for the U-234, -233 determination in Sample 1, there definitely appears to be a bias in either the single-laboratory evaluation, which was used to arrive at the reference value, or the collaborative study results.

An objective of the present study was to determine if the precision of the measured uranium concentrations approached the precision expected from counting statistics. The standard deviations expected from counting statistics errors were calculated from the total counts and total counting time of each duplicate determination which were supplied by the participating laboratories. They are given in Table 11, along with the standard deviation of the uranium concentrations determined in each sample. It can be seen that the errors calculated from the collaborative study approach the errors expected from counting statistics for Samples 1, 2 and 3. However, for Sample 4, which contained sediment, the collaborative study error was found to be about a factor of 2.5 higher than the error expected from counting statistics. Thus, when the present procedure is applied to water samples which do not contain sediment, the precision of the results approaches counting statistics errors.

The collaborative study results shown in Table 11 agree to within 5% of the reference values, except when the very low uranium concentrations resulted in high errors due to counting statistics. These low-level determinations showed that as little as 0.1 dpm/l could be detected by this method.

In conclusion, the uranium-in-water procedure used in the present study gave good results for both the single-laboratory and multilaboratory evaluations. It is believed that this method provides a relatively simple, cost effective means of accurately determining uranium isotopes in water.

TABLE 11. OVERALL STANDARD DEVIATION OF COLLABORATIVE STUDY RESULTS AND STANDARD DEVIATIONS EXPECTED FROM COUNTING STATISTICS ERRORS

Sample Number	Isotope	Avg Uranium Concn (dpm/l)	Std Dev of Data (dpm/l)	Std Deviations Expected From Counting Statistics (dpm/l)
1	U-238	2136	±47 (2.3%)	±47 (2.3%)
1	U-234, -233	1610	±36 (2.1%)	±40 (2.4%)
1	U-235, -236	112	±24 (21%)	±10 (9%)
2	U-238	0.12	±0.03 (25%)	±0.02 (17%)
2	U-234, -233	13.60	±0.32 (2.4%)	±0.33 (2.4%)
2	U-235, -236	0.040	±0.021 (53%)	±0.016 (40%)
3	U-238	1.69	±0.07 (4.1%)	±0.09 (5.2%)
3	U-234, -233	1.71	±0.05 (2.9%)	±0.09 (5.2%)
3	U-235, -236	0.073	±0.023 (32%)	±0.020 (27%)
4	U-238	55.4	±3.1 (5.5%)	±1.3 (2.3%)
4	U-234, -233	54.8	±3.1 (5.5%)	±1.3 (2.3%)
4	U-235, -236	2.84	±0.41 (14%)	±0.16 (5.6%)

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APPENDIX 1
TENTATIVE METHOD FOR THE DETERMINATION OF URANIUM ISOTOPES IN WATER (BY A COPRECIPITATION ANION EXCHANGE TECHNIQUE)

This appendix is a reprint of a procedure of the same title by Carl T. Bishop, Vito R. Casella, Ralph Brown, Antonia A. Glosby, and Bob Robinson* of Mound Facility in Miamisburg, Ohio. The report was prepared February 14, 1977, for the U. S. Environmental Protection Agency under Contract No. EPA-IAG-D6-0015. Mound Facility is operated by Monsanto Research Corporation for the U. S. Department of Energy† under U. S. Government Contract No. EY-76-C-04-0053. The procedure was prepared by Mound Facility for distribution to participants in the interlaboratory collaborative study and was designated as report number MLM-MU-77-61-0001.

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PREFACE

The analytical procedure described in this document is a tentative method for the determination of uranium isotopes in water. It is being collaboratively tested according to an interagency agreement between the U. S. Environmental Protection Agency (USEPA) and the U. S. Energy Research and Development Administration (USERDA)*. Data from the collaborative test will be examined and information on the precision and accuracy of the method will be obtained. A final report describing the results of the collaborative study will be prepared.

*Effective October 1, 1977 U. S. Energy Research and Development Administration was designated the Department of Energy.

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1. SCOPE AND APPLICATION

1.1 General Considerations

This procedure applies to the determination of uranium isotopes in fresh water and in seawater. It has been applied to fresh water samples having a volume as high as 20 liters. The volume of seawater that can be analyzed by this method is limited by the fact that a seawater sample must be boiled before analysis, thus seawater analysis is usually limited to a few liters. This method applies to soluble uranium as well as to any uranium that might be present in suspended matter in the water sample. When suspended matter is present, a nitric acid-hydrofluoric acid dissolution step is added to the procedure to assure that the uranium present in the suspended matter completely dissolves.

The method described in this procedure can be carried out by an experienced technician under the supervision of a chemist who fully understands the concepts involved in the analysis. It involves relatively simple operations, but it should be utilized only after satisfactory results are obtained by the analyst when replicate standard samples are analyzed.

1.2 Minimum Detectable Activity

The minimum detectable concentration of a given uranium isotope in water is dependent upon the volume of water analyzed and the minimum detectable activity (MDA) of the isotope. In a given laboratory situation this will also depend upon the observed blank values (cf. Section 3). The MDA is defined as that amount of activity which in the same counting time, gives a count which is different from the background count by three times the standard deviation of the background count.

The MDA can be calculated from some typical parameters that might be expected from the method described in this procedure. Suppose a sample is counted for 1,000 minutes using a silicon surface barrier detector with a 25% counting efficiency, the background in the energy region

of interest is 5 counts in 1000 minutes, and the chemical recovery of the uranium tracer is 80%. From the definition of the MDA, the sample count would have to be seven (ca. $3 \times \sqrt{5}$), in 1000 minutes, and to achieve this count under the stated conditions would require 0.034 d/m of activity. Thus, a typical MDA for a given uranium isotope in water by this procedure would be 0.03 d/m.

1.3 Sensitivity

From the minimum detectable activity computed in the last section, the sensitivity of this isotopic method can be compared to that of a fluorometric method recommended by the EPA for uranium in drinking water (ASTM, 1976). This fluorometric method is used for determining total uranium in the concentration range from 0.005 to 50 mg/liter. The method described in this procedure is an isotopic method, in which uranium isotopes are detected by alpha pulse height analysis. The long lived isotopes of uranium along with some of these properties of interest to this procedure are given in Table 1. Generally the fluorometric method is able to detect only uranium-238 in environmental samples

TABLE 1

PROPERTIES OF URANIUM ISOTOPES
OF INTEREST IN ENVIRONMENTAL SAMPLES

Isotope	Half-Life (Years)	Specific Activity (dis/min/μg)	Alpha Energies in MeV (Abundance)
U-232	72	4.75×10^{7}	5.32 (68%), 5.27 (32%)
U-233	1.62×10^{5}	21,030	4.82 (83%), 4.78 (15%)
U-234	2.47×10^{5}	13,730	4.77 (72%), 4.72 (28%)
U-235	7.1×10^{8}	4.756	4.58 (8%), 4.40 (57%) 4.37 (18%)
U-236	2.39×10^{7}	140.7	4.49 (76%), 4.44 (24%)
U-238	4.51×10^{9}	0.7393	4.20 (75%), 4.15 (25%)

since the mass concentrations of the other uranium isotopes are not high enough to be determined by this chemical method. It can be seen from Table 1, however, that the specific activities of all of the other isotopes of uranium are higher than the specific activity of uranium-238. Thus, this isotopic method can be used to detect much smaller masses of these other uranium isotopes, because the measurement of the radioactivity is much more sensitive for these isotopes with high specific activities.

To make a quantitative comparison between the above fluorometric method and the present isotopic method, a particular isotope has to be chosen for comparison. Since the fluorometric method applies essentially to uranium-238, a comparison is made on the basis of this isotope. Using the minimum detectable activity computed in Section 1.2 and considering a 3-liter water sample, the lowest concentration of uranium-238, in µg/liter, that could be detected by the isotopic method would be:

$$0.034 \text{ d/m} \Big/ \left(0.739 \frac{\text{d/m}}{\mu\text{g}} \times 3 \text{ liter}\right)$$

$$= 0.015 \text{ µg/liter}.$$

Comparing this number to the lower end of the concentration range given for the ASTM fluorometric method, the isotopic method is more sensitive by better than two orders of magnitude than the former method. On the other hand a sensitivity of better than 0.05 µg/liter has been reported for uranium-238 (Montgomery, 1977) using another fluorometric method (Barker, 1965).

Although fluorometric methods are comparable in sensitivity to counting methods for uranium-238 (natural uranium), fluorometric methods could not detect other uranium isotopes which are readily detectable by counting methods. When determining uranium in water as a radioactive contaminant, it seems only logical that an isotopic method be the preferred method of use.

1.4 Precision and Accuracy

The precision of the method has not yet been evaluated, but based on experience with a similar procedure for plutonium in water, the precision is expected to approach that of counting statistics errors. The accuracy is expected to be within the limits propagated from counting statistics and the uncertainty in the specific activity of the tracer used.

2. SUMMARY

The present procedure involves coprecipitation of uranium with ferrous hydroxide, a nitric-hydrofluoric acid dissolution if the sample contains sediment, separation of the uranium by anion exchange in hydrochloric acid, electrodeposition and alpha pulse height analysis.

The sample is acidified to pH 1 and uranium-232 (not normally found in environmental samples) is added to serve as an isotopic tracer before any additional operations are carried out. If the sample is a seawater sample, or if it contains carbonate or bicarbonate ions, the sample must be boiled under acid conditions to convert these ions to carbon dioxide gas which is then expelled from the solution. Carbonate ions cannot be present during the precipitation step since they complex the uranium and prevent its coprecipitation. The uranium is coprecipitated from the sample by adding sodium bisulfite, iron chloride solution and adjusting the pH to 10 with concentrated ammonium hydroxide. The ferrous hydroxide precipitate is dissolved in concentrated hydrochloric acid, or is subjected to an acid dissolution with concentrated nitric and hydrofluoric acids if the hydrochloric acid fails to dissolve the precipitate.

The sample is adjusted to a concentration of 8 M in hydrochloric acid and passed through an anion exchange resin column. The uranium will be strongly absorbed on the resin at this hydrochloric acid concentration. Polonium and bismuth will also be absorbed while thorium and radium will pass through the column. Plutonium and iron are also retained by the resin, but are eluted with 6 M HCl containing hydrogen iodide. The iodide ion reduces the plutonium (IV) to plutonium (III) and reduces the iron (III) to iron (II), and neither of these ions is retained by the ion exchange resin in 6 M HCl. The uranium is eluted from the column with 0.1 M HCl and is then electrodeposited on

a stainless steel slide for counting by alpha pulse height analysis using a silicon surface barrier detector.

When uranium-232 is used as a tracer, the other isotopes of uranium listed in Table 1 can be detected in the alpha spectrum of an unknown sample. From the alpha energies given in Table 1 it can be seen that the alpha energy of uranium-232 is at least 0.50 MeV higher than the energy of any other uranium isotope. Thus, there should be little interference from tailing of the uranium-232 into the lower energy alpha peaks. If a sample contained both uranium-233 and uranium-234, it would be very difficult to resolve these two peaks since their principal alpha energies differ by only 0.05 MeV. The other uranium peaks can be resolved if the resolution is good.

3. INTERFERENCES

3.1 The only possible alpha activity that may come through the chemistry of the procedure is protactinium-231 (Edwards, 1968). Protactinium-231 has the following alpha energies in MeV, the abundance being given in parentheses: 5.06 (10%), 5.02 (23%), 5.01 (24%), 4.95 (22%) and 4.73 (11%). Thus, from Table 1, it can be seen that this protactinium-231 could possibly interfere with the determination of uranium-233 or uranium-234.

3.2 In determining very low levels of uranium isotopes in environmental samples, detector backgrounds and laboratory blanks must be accurately determined. Blank determinations must be made in order to ascertain that the contamination from reagents, glassware and other laboratory apparatus is negligible compared to the sample that is being analyzed. A blank determination should be made in exactly the same way a sample determination is made. For accurate analyses blank determinations should be consistent, and should be an order of magnitude lower than activities obtained when analyzing samples.

4. APPARATUS

4.1 Instrumentation

4.1.1 Alpha Pulse Height Analysis System - A system consisting of a silicon surface barrier detector capable of giving a resolution of 50 keV or better with samples electrodeposited on flat mirror-finished stainless steel slides. The resolution here is defined as the width of the alpha peak in keV, when the counts on either side of the peak are equal to one-half of the counts at the maximum of the peak. The counting efficiency of the system should be greater than 15% and the background in the energy region of each peak should be less than 10 counts in 1,000 minutes.

4.1.2 Electrodeposition Apparatus - A direct current power supply, 0 to 12 volts and 0 to 2 amps, is required for the electrodeposition described in this procedure. A disposable electrodeposition cell is also recommended. An apparatus similar to that shown in Figure 1 has been used in the present procedure. In the present procedure, the cell itself is surrounded by water, but the water is not circulated. The electrodeposition can be carried out without the water cooling. The cathode is a stainless steel slide with a polished mirror finish. The diameter of the slide is 1.91 cm (3/4 in.) and the thickness is ca. 0.05 cm (0.02 in.). The exposed cathode area during electrodeposition is 2 cm^2.

The anode is a 1-mm diameter platinum wire with an 8-mm diameter loop at the end above the cathode.

4.2 Laboratory Equipment

4.2.1 Balance - top loading, capacity 1,200 g, precision $\pm$ 0.1 g.

4.2.2 Hot plate - magnetic stirrer and stirrer bar.

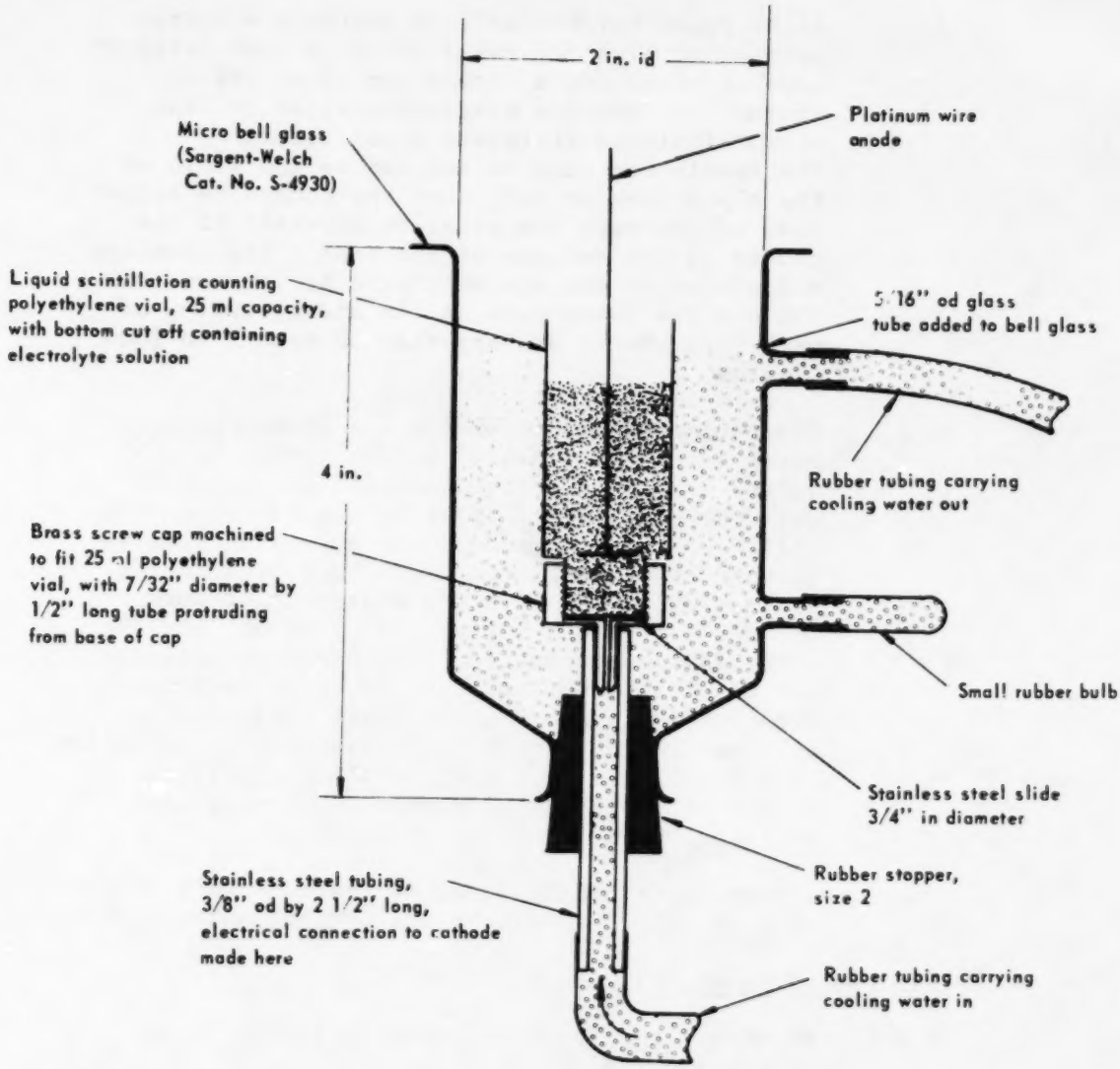

Figure 1. Water Cooled Electrodeposition Apparatus

4.2.3 Peristaltic pump with pumping capacity of 4 liters per minute (required only for samples of several liters or greater).

4.2.4 Centrifuge - capable of handling 100 ml or larger centrifuge bottles (a larger centrifuge is required for handling 10 liter or larger samples).

4.3 Labware

4.3.1 Graduated cylinders - 5 ml to 1,000 ml.

4.3.2 Beakers - glass, 100 ml to 2 liters.

4.3.3 Beakers - teflon, 250 ml with teflon covers.

4.3.4 pH paper - pH range 2 to 10.

4.3.5 Automatic pipettes - with disposable tips, volumes between 100λ and 1,000λ.

4.3.6 Centrifuge bottles - 100 ml or greater (larger bottles are required for 10 liter or larger samples).

4.3.7 Ion exchange columns - approximately 1.3 cm i.d. 15 cm long with 100-ml reservoir.

4.3.8 Pipettes - glass, Class A.

4.3.9 Disposable pipettes - 2-ml glass eye-dropper type, with rubber bulb.

4.3.10 Dropping bottles.

4.3.11 Watch glasses.

4.3.12 Polyethylene washing bottles.

4.3.13 Glass stirring rods.

4.3.14 Safety glasses or goggles.

4.3.15 Rubber gloves.

4.3.16 Crucible tongs - platinum tipped.

4.3.17 Beaker tongs.

4.3.18 Spatulas.

4.3.19 Heat lamp-mounted on ring stand for drying slides.

5. STANDARDS, ACIDS, REAGENTS

5.1 Standards

5.1.1 Standardized uranium-232 solution.

5.2 Acids

Reagent grade, meeting American Chemical Society (ACS) specifications; diluted solutions prepared with distilled deionized water.

5.2.1 Nitric acid - concentrated (16 M).

5.2.2 Hydrochloric acid - concentrated (12 M), 8 M, 6 M, 0.5 M, 0.1 M.

5.2.3 Sulfuric acid - concentrated (18 M), 1.8 M.

5.2.4 Hydrofluoric acid - concentrated (48% solution).

5.2.5 Hydriodic acid - concentrated (48% solution).

5.3 Reagents

Reagent grade, meeting ACS specifications; solutions prepared with distilled deionized water.

5.3.1 Ferric chloride - in 0.5 HCl containing 10 mg of iron per ml of solution.

5.3.2 Ammonium hydroxide - concentrated (15 M), 1.5 M, 0.15 M.

5.3.3 Anion exchange resin - Bio Rad AG1-X4 (100-200 mesh) chloride form. (Available from Bio Rad. Laboratories, 3rd and Griffin Avenues, Richmond, California, 94804). A column is prepared by slurrying this resin with 8 M HCl and pouring it onto a column of inside diameter approximately 1.3 cm. The height of the column of resin should be about 8 cm or greater for samples containing suspended matter or for large volume samples.

5.3.4 Sodium hydrogen sulfite

5.3.5 Sodium hydrogen sulfate solution ca. 5% in 9 M H_2SO_4; dissolve 10 g of the $NaHSO_4 \cdot H_2O$ in 100 ml of water and then carefully add 100 ml of 18 M H_2SO_4.

5.3.6 Preadjusted electrolyte - 1 M ammonium sulfate adjusted to pH 3.5 with 15 M NH_4OH and 18 M H_2SO_4.

5.3.7 Thymol blue indicator, sodium salt (available from Fisher Scientific Company) - 0.04% solution.

5.3.8 Ethyl alcohol - made slightly basic with a few drops of 15 M NH_4OH per 100 ml of alcohol.

6. CALIBRATION AND STANDARDIZATION

6.1 Standardization of the Uranium-232 Tracer Solution

If a standard uranium-232 solution is not available, a freshly purified sample of uranium-232 could be standardized by mixing a known amount of another standard solution such as uranium-236, with a known amount of the solution to be standardized, mixing thoroughly and electroplating the mixture. From an alpha pulse height analysis of the mixture

the specific activity of the uranium-232 solution could be determined. Alternately, a freshly purified solution of uranium-232 could be standardized by 2π counting. Weighed aliquots of the solution free of hydrochloric acid could be evaporated on platinum or stainless steel slides and counted with a 2π proportional counter. The efficiency of the 2π proportional counter can be accurately determined with a National Bureau of Standards alpha-particle standard. When using these standards, corrections for resolving time and backscattering must be made if necessary.

6.2 Determination of Alpha Spectrometer Efficiency

Determination of the alpha spectrometer counting efficiency is not necessary to get an accurate concentration of the uranium isotopes in the water sample being analyzed, since the counting efficiency of the electroplated sample is the same for the tracer uranium isotope and for the unknown uranium isotope. This efficiency cancels out when the concentration of the unknown uranium isotope is calculated (cf. Section 8.1). A determination of the alpha spectrometer counting efficiency is required to calculate the uranium recovery of a particular analysis. To determine this efficiency requires that one count an alpha particle source of known alpha particle emission rate under the same conditions that the samples are counted. The alpha particle counting efficiency is then calculated as illustrated in Section 8.2.

7. STEP BY STEP PROCEDURE FOR ANALYSIS

7.1 Coprecipitation

7.1.1 Weigh or measure the volume of a 1-liter or larger water sample.

7.1.2 If the sample has not been acidified, add 5 ml of 12 M HCl per liter of sample.

7.1.3 Mix the sample completely using a magnetic stirrer for small samples, or a peristaltic or other pump for larger samples. Check the acidity with pH paper. If the pH is greater than 1, add 12 M HCl until it reaches this value.

7.1.4 Add standardized uranium-232 tracer with a calibrated pipette (or add a weighed amount of the tracer) to give about 10 d/m of uranium-232.

7.1.5 Mix the sample for about 1 hour or longer if the sample volume is greater than a few liters. (If the sample volume is only a few liters, it is advisable to heat the water to near boiling while stirring.)

7.1.6 If the sample is a seawater sample or contains carbonate ions, it must be boiled for about 5 minutes. The pH must be checked again after boiling and, if it is greater than 1, 12 M HCl must be added to bring it back to 1.

7.1.7 Add about 250 mg of $NaHSO_3$ and 20 mg of iron as $FeCl_3$ in 0.5 M HCl to a 1-liter sample. Add up to 2 g of $NaHSO_3$ and up to 500 mg of iron for larger samples.

7.1.8 Stir again for 10 minutes or longer if the sample volume is greater than a few liters. (If the sample volume is only a few liters or less, heat the sample to boiling.)

7.1.9 Add 15 M NH_4OH while stirring to precipitate the iron. Continue adding 15 M NH_4OH to raise the pH to 9 to 10 as determined with pH paper.

7.1.10 Continue to stir the sample for 30 minutes, or longer for samples with a volume greater than a few liters, before allowing it to settle.

7.1.11 After the sample has settled sufficiently, decant the supernate, being careful not to remove any precipitate. (If the analyst wishes to continue immediately, the iron hydroxide may be filtered out at this time.)

7.1.12 Slurry the remaining precipitate and supernate and transfer to a centrifuge bottle. If larger samples of water are being analyzed, it may be necessary to transfer the slurry to a large beaker and allow it to settle again.

7.1.13 Centrifuge the sample and pour off the remaining supernate.

7.1.14 Attempt to dissolve the precipitate with a minimum volume of 12 M HCl. If the precipitate dissolves completely, add a volume of 12 M HCl equal to twice the volume of the sample solution and dilute to 100 to 150 ml with 8 M HCl, or otherwise adjust the acidity to 8 M HCl. For a sample that does dissolve, proceed to Section 7.3, Anion Exchange Separation. If the sample does not dissolve in the 12 M HCl, evaporate to dryness, heat to 450°C for a few hours and proceed to the next section, Section 7.2, Acid Dissolution of Insoluble Residue.

7.2 Acid Dissolution of Insoluble Residue

7.2.1 Transfer the sample that did not dissolve in the 12 M HCl to a 250-ml Teflon beaker and add 60 ml of 16 M HNO_3 and 30 ml of 48% HF.

(CAUTION: HF is very hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills and wash thoroughly after using HF).

7.2.2 Place the sample on a magnetic stirrer hot plate, add a Teflon-coated stirring bar, (cover with a Teflon sheet), and digest for about 2 hours while stirring. If the volume drops below about 25 ml, add equal volumes of 16 M HNO_3 and 48% HF (cooling the sample somewhat before adding).

7.2.3 Remove the sample from the hotplate and cool to near room temperature (30 to 40°C). Add 20 ml of 12 M HCl and slowly take the sample to dryness on the hotplate. Remove the beaker from the hotplate as soon as it has dried.

7.2.4 Cool the sample to near room temperature. Add 50 ml of 8 M HCl and boil gently for a few minutes.

7.2.5 Filter through a Whatman No. 40 filter paper and wash the paper with about 10 ml of 8 M HCl, combining the wash water with the filtrate. Take this solution and proceed with Section 7.3, Anion Exchange Separation.

7.3 Anion Exchange Separation

7.3.1 Condition the anion exchange resin column (prepared as described in Section 5.3) by rinsing the column with 4 column volumes of 8 M HCl.

7.3.2 Transfer the sample from Step 7.1.14 or Step 7.2.5 to the conditioned anion exchange resin.

7.3.3 After the sample has passed through the column, elute the iron (and plutonium if present) with six column volumes of 6 M HCl containing 1 ml of concentrated HI per 9 ml of 6 M HCl (freshly prepared).

7.3.4 Rinse the column with two additional six column volumes of 6 M HCl.

7.3.5 Elute the uranium with six column volumes of 0.1 M HCl.

7.3.6 Evaporate the sample to about 20 ml and add 5 ml of 16 M HNO_3.

7.3.7 Evaporate the sample to near dryness.

7.4 Electrodeposition

7.4.1 Add 2 ml of a 5% solution of $NaHSO_4 \cdot H_2O$ in 9 M H_2SO_4 to the sample.

7.4.2 Add 5 ml of 16 M HNO_3, mix well and evaporate to dryness, but do not bake.

7.4.3 Dissolve the sample in 5 ml of the preadjusted electrolyte (cf. Section 5.3), warming to hasten the dissolution.

7.4.4 Transfer the solution to the electrodeposition cell using an additional 5 to 10 ml of the electrolyte in small increments to rinse the sample container.

7.4.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H_2SO_4 (or 15 M NH_4OH) until this color is obtained.

7.4.6 Place the platinum anode into the solution so that it is about 1 cm above the stainless steel slide which serves as the cathode.

7.4.7 Connect the electrodes to the source of current, turn the power on, and adjust the power supply to give a current of 1.2 amps. (Constant current power supplies will require no further adjustments during the electrodeposition).

7.4.8 Continue the electrodeposition for 1 hour.

7.4.9 When the electrodeposition is to be terminated, add 1 ml of 15 M NH_4OH and continue the electrodeposition for 1 minute.

7.4.10 Remove the anode from the cell and then turn off the power.

7.4.11 Discard the solution in the cell and rinse the cell 2 or 3 times with 0.15 M HN_4OH.

7.4.12 Disassemble the cell and wash the slide with ethyl alcohol that has been made basic with NH_4OH.

7.4.13 Touch the edge of the slide to a tissue to absorb the alcohol from the slide.

7.4.14 Dry the slide, place it in a box and label for counting. (The sample should be counted within a week, since uranium-232 daughters grow into the sample and possibly interfere with the determination of certain other uranium activities.)

7.5 Alpha Pulse Height Analysis

7.5.1 Count the samples for at least 1,000 minutes or longer if the detector efficiency is less than 15%, if the tracer recovery is low, or if the unknown uranium activity is low.

7.5.2 Check the alpha pulse height analysis spectrum for peaks at the uranium-233, uranium-234, uranium-235, uranium-236 and/or uranium-238 alpha energies (see Table 1) and determine the total counts in each peak. Where two isotopes are close in energy, complete resolution may not be possible. (This is the case with uranium-234 and uranium-235, for example.)

7.5.3 Make the necessary background corrections. (The background should be determined by a 4,000-minute or longer count.)

7.5.4 Make a blank correction for each peak, if necessary.

8. CALCULATION OF RESULTS

8.1 Calculations of Uranium Concentrations in Water

By integrating the appropriate energy peak along with the uranium-232 tracer peak, the concentrations of the corresponding uranium isotope can be determined (cf. Table 1). This concentration is calculated as follows:

$$X_i = \frac{C_i \times A_t}{C_t \times V_s} \qquad (8.1)$$

where X_i = the concentration of the unknown uranium isotope in the water in disintegrations per minute (d/m) per liter.

C_i = the net sample counts in the energy region corresponding to the uranium isotope being measured.

A_t = the activity of the uranium-232 tracer added to the sample in d/m.

C_t = the net sample counts in the uranium-232 tracer energy region of the alpha spectrum.

V_s = the volume in liters, of the water sample taken for analysis.

8.2 Calculation of Alpha Spectrometer Efficiency

The absolute counting efficiency of the alpha spectrometer, ε, must be determined in order to calculate the uranium recovery of the analytical procedure.

To determine this efficiency requires a standard source of a known alpha particle emission rate:

$$\varepsilon = R_s/R_\alpha \qquad (8.2)$$

where R_s = the net counting rate of the standard source in the energy region of the alpha emitter of interest in counts per minute.

R_α = the absolute alpha particle emission rate of the alpha emitter of interest in alpha disintegrations per minute.

8.3 Calculation of Uranium Recovery of the Chemical Analysis

The uranium recovery efficiency E (%) expressed in percent is given by:

$$E(\%) = \frac{C_t \times 100\%}{t \times A_t \times \varepsilon} \qquad (8.3)$$

where t=the counting time in minutes. The other terms are as defined in Sections 8.1 and 8.2.

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APPENDIX 2
COLLABORATIVE STUDY INSTRUCTIONS-URANIUM IN WATER
(March 1977)

1. Use the procedure, "Tentative Method for the Determination of Uranium Isotopes in Water (By a Coprecipitation Anion Exchange Technique)." February 14, 1977.

2. If you have not used a procedure similar to the one enclosed, it would be advisable to analyze a few known samples before analyzing the test samples.

3. If you do not have the ion exchange resin or other reagents needed for the analysis of the test samples, Mound Facility will furnish them if you desire. Contacts are given below.

4. Use care in opening the samples. They were shipped in collapsible containers and may tend to overflow when opened. Samples may be less than 1 liter in volume, but this does not matter; measure the weight or volume of samples 77-1, 77-2 and 77-3. When analyzing sample 77-4, quantitatively transfer the entire contents of the sample to a larger beaker for analysis.

5. Additional amounts of any sample are available if a sample is spilled, an obviously incorrect uranium concentration is obtained, etc. Contacts are given below.

6. The coprecipitation step in the procedure (step 7.1) may be omitted for sample 77-1; instead after weighing the sample and adding the U-232 tracer, the sample should be evaporated on a hotplate to dryness and about 20 ml of 8 M HCl should then be added for the anion exchange separation (step 7.3). Since the uranium concentration for this sample is quite high (1,000-2,500 dis/min/liter), only 5 to 25 ml are necessary for each determination. Excess sample is provided so that practice runs can be made if desired. Although only one container of sample 77-1 is provided, duplicate analyses should be determined.

7. Sample concentrations of 77-2, 77-3 and 77-4 are in the range 0.5 to 100 dis/min/liter; therefore, the total sample (~1 liter) should be used for each analysis. Blanks should be made in your laboratory to be certain that the samples are not a problem at this uranium concentration.

8. We are requesting that the same tracer, U-7, be used by all participants. Using 1 ml of this tracer gives the approximate amount of U-232 called for in the procedure. if you dilute the tracer supplied, keep in mind that it is in a 1 M HNO_3 solution.

9. In this collaborative test, the acid dissolution procedure (Section 7.2) will be required only on sample 77-4.

10. The electrodeposition apparatus shown in Figure 1 of the procedure is only an illustration. Your apparatus should be similar, but not necessarily the same.

11. All samples should be counted for at least 1,000 minutes.

12. Individual counting data are requested so that the counting statistics error can be resolved from other errors.

13. Sample 77-2 contains 0.3 dis/min/liter of U-232. An appropriate tracer correction is necessary for determining other uranium isotopes; that is, for equation 8.1 in the procedure $A_t' = A_t + 0.3V_s$, where A_t' is the total activity of U-232 for this sample.

14. Only one ampoule of U-232 tracer is provided (enough for 9 to 10 determinations), but more tracer will be provided if necessary.

15. The densities may be required in order to report the results in dis/min/liter. They are as follows: 77-1 (1.028 g/cm^3), 77-2 (1.017 g/cm^3) and 77-3 (1.040 g/cm^3).

APPENDIX 3
DATA ON URANIUM-232 TRACER

Isotope: U-232 I.D. No.: U-7

Date Prepared: 1/25/77

Specific Activity: 12.75 dpm/gram (±1.5%) (on date prepared)
13.15 dpm/cm^3

Density: 1.031 g/cm^3 at 20°C

Acid Medium: 1 M HNO_3

Source: U. S. Department of Energy, Environmental Measurements Laboratory, purified by ion exchange and standardized at Mound Facility.

Half Life: 72 years

Opening Instructions: The constriction of the glass ampoule has been previously scored and reinforced with a blue ceramic band. It can readily be broken without a file. The small polyethylene bottle with the long narrow neck, enclosed with the ampoule, may be used to remove the tracer from the opened ampoule and for weighing the amount of tracer added to each sample.

Prepared At: Mound Facility
Monsanto Research Corporation
Miamisburg, Ohio 45342

APPENDIX 4
LABORATORIES PARTICIPATING IN THE URANIUM-IN-WATER COLLABORATIVE STUDY

Eberline Albuquerque Laboratory
Albuquerque, New Mexico

LFE Environmental Analysis Laboratories
Richmond, California

New York State Department of Health
Albany, New York

Teledyne Isotopes
Westwood, New Jersey

U. S. Department of Energy
Environmental Measurements Laboratory
New York, New York

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory - Cincinnati
Cincinnati, Ohio

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory - Las Vegas
Las Vegas, Nevada

Westinghouse Electric Corporation
Advanced Reactors Division
Madison, Pennsylvania